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PATENT

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FOR: PLASMA DISPLAY PANEL DEVICE AND METHOD OF  
FABRICATING PHOSPHOR THEREFORVERIFICATION OF A TRANSLATION

Assistant Commissioner for Patents

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PLASMA DISPLAY PANEL DEVICE AND METHOD OF  
FABRICATING PHOSPHOR THEREFOR.

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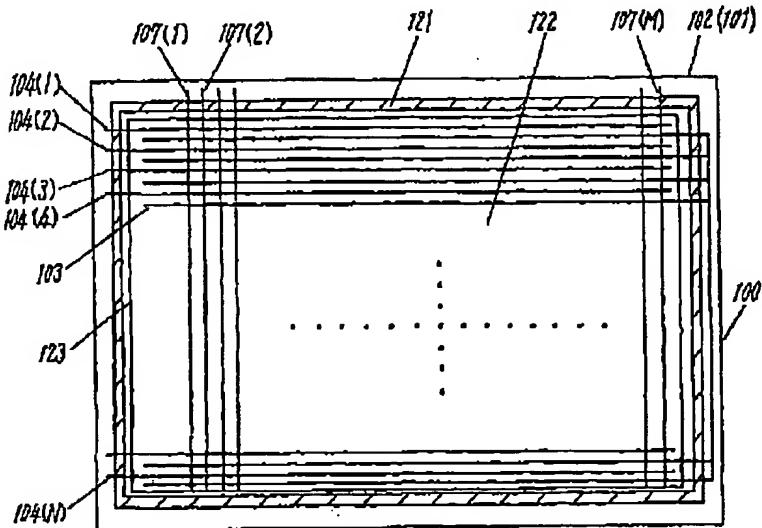
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(54) Title: PLASMA DISPLAY APPARATUS, FLUORESCENT MATERIAL, AND FLUORESCENT MATERIAL MANUFACTURING METHOD

(54) 発明の名称: プラズマディスプレイ装置及び蛍光体及び蛍光体の製造方法



A1

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(57) Abstract: Adsorption of water by the surface of a blue fluorescent material is suppressed, and degradation in luminance, change in chromaticity or discharge characteristic of the fluorescent material is improved. In a plasma display device, adsorption of water by the surface of the blue fluorescent material is suppressed, and degradation in luminance, change in chromaticity or discharge characteristic of the fluorescent material is improved by using the fluorescent material in which trivalent Eu ions are substituted for a part of bivalent Eu ions in the blue fluorescent material to eliminate oxygen defects in the vicinity of a layer (Ba-O layer) containing Ba atoms of the blue fluorescent material.

[統案有]

[Name of the Document] Specification

[Title of the Invention] Phosphor, phosphor manufacturing method, and plasma display unit.

[Claims]

[Claim 1] A method of manufacturing a phosphor having a luminescence center that is at least one of Eu and Mn added as an activator and base crystal that is composite oxide containing at least one of elements such as Ba, Ca, Sr, and Mg, at least comprising the steps of:

treatment in a reduction atmosphere for burning a mixed material of the phosphor in a reduction atmosphere by once at least; and

treatment in an ozone atmosphere for treating the mixed material in an ozone atmosphere which is executed after the step of the treatment in a reduction atmosphere.

[Claim 2] A phosphor obtained by the method of manufacturing a phosphor of claim 1, wherein the composition formula of the phosphor is  $Ba_{(1-y)}Sr_yMgAl_{10}O_{17}:Eu_x$  (where  $0.01 \leq x \leq 0.20$ ,  $0 \leq y \leq 0.30$ ).

[Claim 3] A plasma display unit with a plurality of single-color or multi-color discharge cells disposed therein and phosphor layers corresponding to the colors of the discharge cells disposed therein, wherein the phosphor layers are excited by ultra-violet rays to emit light, and at least one of the phosphor layers contains the phosphor of claim 2.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to a phosphor and a method of

manufacturing a phosphor, and particularly, the phosphor is preferably usable for image display units such as a plasma display unit, and for illuminating devices such as a rare gas discharge lamp and high-load fluorescent lamp.

[0002]

[Background Art]

Recently, in a color display device used for image display such as a computer and television, a plasma display unit is spotlighted as a color display device capable of realizing a large-sized, thin and light-weight device.

[0003]

A plasma display unit performs full-color display by additive color mixing of the three primary colors (red, green, blue). For realizing the full-color display, a plasma display unit is provided with phosphor layers for emitting the respective three primary colors red, green and blue. And, in the discharge cell of the plasma display unit, ultraviolet ray of 200 nm or less in wavelength is generated by discharging a rare gas, and the ultraviolet ray excites the phosphors of respective colors to produce visible light of respective colors.

[0004]

As the color phosphors, for example, (Y, Gd) BO<sub>3</sub>: Eu<sup>3+</sup>, Y<sub>2</sub>O<sub>2</sub>S: Eu<sup>3+</sup> for emitting a red color, (Ba, sr, Mg) O·aAl<sub>2</sub>O<sub>3</sub>: Mn<sup>2+</sup>, Zn<sub>2</sub>SiO<sub>4</sub>: Mn<sup>2+</sup> for emitting a green color, and BaMgAl<sub>10</sub>O<sub>17</sub>: Eu<sup>2+</sup> for emitting a blue color are commonly known.

[0005]

Out of these, for a blue phosphor that is a phosphor whose base material is  $\text{BaMgAl}_{10}\text{O}_{17}$  called BAM type, Eu, luminescence center, has to be subjected to bivalent activation in order to enhance the emission luminance, which is therefore manufactured by burning in a reduction atmosphere (for example, refer to non-patent document 1). This is because, if the phosphor is burned in an oxidation atmosphere, Eu will become trivalent, and Eu cannot substitute for the position of bivalent Ba in the base crystal, and as a result, it is unable to become an active luminescence center, causing the emission luminance to be decreased. Further, it fails to achieve the original purpose of blue phosphor and emits red light peculiar to  $\text{Eu}^{3+}$ .

[0006]

Also, for a red phosphor that is europium-activated yttrium oxysulfide ( $\text{Y}_2\text{O}_2\text{S}$ :  $\text{Eu}^{3+}$ ), Eu has to be activated trivalent, which is therefore manufactured by burning in an oxidation atmosphere. On the other hand, for a phosphor whose base crystal is formed of oxide, it can be considered that oxygen atoms are taken away from the base crystal during burning, causing oxygen fault to take place in the phosphor. As a method of improving such oxygen fault, a method of burning  $\text{Y}_2\text{O}_2\text{S}$ :  $\text{Eu}^{3+}$  wherein Eu is subjected to trivalent activation by using an inert gas containing oxygen is disclosed (refer to Patent document 1).

[0007]

[Patent document 1]

"Phosphor Handbook" edited by Phosphor Research Society, Ohmsha,

p170.

## [Patent document 1]

Japanese Laid-Open Patent 2000-290649 (page 2 to 3).

## [0008]

## [Problems to be Solved by the Invention]

However, as compared with oxide phosphor manufactured by burning in an oxidation atmosphere, in the case of oxide phosphor manufactured by burning in a reduction atmosphere, oxygen fault increases in the base crystal because oxygen is liable to be taken away from base crystal in a reduction atmosphere. Further, when oxide phosphor to be burned in a reduction atmosphere is burned in an oxidation atmosphere, there arises a problem that it is difficult to keep the original valences of the activator.

## [0009]

That is, in case a phosphor having considerable oxygen fault in base material is subjected to ion impact due to application or discharge of high-energy ultraviolet ray (147 nm in wavelength) generated by a plasma display unit, the phosphor is liable to be deteriorated with the lapse of time. This is probably because binding of atoms is weak to each other at the portion of oxygen fault, and if high-energy ultraviolet ray or ion impact is applied thereto, it will cause the crystal structure to be put into disorder, giving rise to non-crystallization. Such a non-crystallized portion means deterioration of the base crystal, and in a plasma display unit, it results in luminance deterioration with the lapse of time, chromatic differences due to change in chromaticity, and image burn or the like.

## [0010]

Also, when an oxide phosphor to be burned in a reduction atmosphere is burned in an oxidation atmosphere for the purpose of improving oxygen fault, in a BAM phosphor, for example, Eu is activated to trivalent Eu<sup>3+</sup>, giving rise to considerable luminance deterioration.

[0011]

The present invention is intended to solve such a problem, and the object of the invention is to provide a method of manufacturing a phosphor wherein oxygen fault can be improved without decreasing the luminance even in the case of a phosphor having oxide as a base crystal for which Eu or Mn being the luminescence center has to be subjected to bivalent activation, a phosphor being high in luminance and less in luminance deterioration, and a plasma display using the same.

[0012]

[Means to Solve the Problems]

The method of manufacturing a phosphor of the present invention is a method of manufacturing a phosphor having a luminescence center that is at least one of Eu and Mn added as an activator and base crystal that is composite oxide containing at least one of elements such as Ba, Ca, Sr, and Mg, at least comprising a step of treatment in a reduction atmosphere for burning a mixed material of the phosphor in a reduction atmosphere by once at least and a step of treatment in an ozone atmosphere for treating the mixed material in an ozone atmosphere which is executed after the step of treatment in a reduction atmosphere. By using such a manufacturing method, oxygen fault of the base crystal generated during the treatment in a reduction atmosphere is improved by the treatment in an ozone atmosphere,

and therefore, it is a method of manufacturing a phosphor being high in luminance and less in luminance deterioration.

[0013]

Also, the phosphor of the present invention is composed of  $\text{Ba}_{(1-x-y)}\text{Sr}_x\text{MgAl}_{10}\text{O}_{17}\text{:Eu}_x$  (where  $0.01 \leq x \leq 0.20$ ,  $0 \leq y \leq 0.30$ ). In such an aluminate phosphor, the above manufacturing method brings about an effect of improving oxygen fault of the base crystal.

[0014]

Also, the plasma display unit of the present invention is a plasma display unit with a plurality of single-color or multi-color discharge cells disposed therein and phosphor layers corresponding to the colors of the discharge cells disposed therein, wherein the phosphor layers are excited by ultraviolet rays to emit light, and at least one of the phosphor layers contains the phosphor. By using such a plasma display unit, it is possible to suppress the generation of luminance deterioration in actual use because the luminance is very high and oxygen fault is less in the base crystal of the phosphor.

[0015]

[Description of the Preferred Embodiments]

The preferred embodiments of the present invention will be described in the following with reference to the drawings.

[0016]

Fig. 1 is a flow chart showing the method of manufacturing a phosphor in the preferred embodiment of the present invention, and the description will be given by using an example of synthesis of  $\text{BaSrMgAl}_{10}$

O<sub>17</sub>: Eu that is one of aluminate phosphors.

[0017]

In step 1, powder weighing step, the following carbonates, oxides, and hydrates are generally used and weighed as materials for individual metals. That is, barium compounds such as barium carbonate, barium hydrate, barium oxide and barium nitrate are used as barium materials. Strontium compounds such as strontium carbonate, strontium hydrate and strontium nitrate are used as strontium materials. Magnesium compounds such as magnesium carbonate, magnesium hydrate, magnesium oxide and magnesium nitrate are used as magnesium materials. Aluminum compounds such as aluminum oxide, aluminum hydrate and aluminum nitrate are used as aluminum materials. Europium compounds such as europium oxide, europium carbonate, europium hydrate and europium nitrate are used as europium materials. These materials are weighed so as to have a predetermined molar ratio of constitutive ions. Each material is not limited to carbonate, oxide or hydrate, and it is preferable to use any compound.

[0018]

In step 2, mixing step, a fluxing agent that is a grain growth accelerator such as aluminum fluoride, barium fluoride, and magnesium fluoride is mixed into the weighed material as needed. As a mixing means, for example, a bowl mill is used for executing about 1 to 5 hours mixing. Also, the material can be mixed by using a bowl mill in a wet method. Besides the use of a bowl mill, it is possible to employ any method such as a coprecipitation method or a method of mixing materials formed from

alkoxide of individual metals in a liquid phase

[0019]

In step 3, filling step, the mixture is filled into a heat-resistant crucible such as a high-purity alumina crucible.

[0020]

In step 4, step of treatment in an ambient atmosphere, the mixed powder filled in the crucible is burned in an ambient atmosphere at temperatures ranging from 800°C to 1500°C for 1 to 10 hours in order to promote the grain growth of the base crystal. Incidentally, step 4 is not an essential step because the purpose is to promote the grain growth.

[0021]

In step 5, step of treatment in a reduction atmosphere, the mixed powder filled in the crucible is burned in a reduction atmosphere, for example, in a nitrogen atmosphere, at a temperature for forming a desired crystal structure. The aluminate phosphor in the preferred embodiment of the present invention is burned in temperatures ranging from 1100°C to 1500°C for 1 to 50 hours.

[0022]

In step 6, step of treatment in an ozone atmosphere, the phosphor powder of a predetermined size is exposed to an ozone atmosphere at temperatures ranging from 350°C to 400°C for 1 to 2 hours. Due to the treatment in such an atmosphere, oxygen atoms get into the oxygen fault of the base crystal generated during the treatment in a reduction atmosphere, thereby improving the oxygen fault.

[0023]

In step 7, step of pulverizing, dispersing, rinsing and drying, the mixed powder treated in an ozone atmosphere is sufficiently dried and then, for example, pulverized, dispersed and rinsed in a wet method for one hour by using a beads mill as a dispersing means. The pulverizing and dispersing method for mixed powder is not limit to beads mill, but it is preferable to use any dispersing device such as a bowl mill and jet mill. After that, the phosphor powder pulverized, dispersed and rinsed is dehydrated and sufficiently dried, followed by predetermined sieving to obtain phosphor powder.

[0024]

In this preferred embodiment, the step of treatment in a reduction atmosphere and the following step of treatment in an ozone atmosphere are performed once each. However, the step of treatment in a reduction atmosphere for enhancing the luminance by bivalent activation of Eu and the step of treatment in an ozone atmosphere for improving oxygen fault of the base crystal can be repeated by a plurality of times. Also, the step of treatment in an ambient atmosphere for promoting the grain growth of base crystal is preferable to be performed once before the step of treatment in a reduction atmosphere. And, it is preferable to pulverize, disperse and rinse the powder after each step of treatment.

[0025]

Fig. 2 is a sectional view of a treatment device in the step of treatment in an ozone atmosphere in the preferred embodiment of the present invention. The temperature of vacuum chamber 41 can be controlled by heater 42, and it can be set to temperatures ranging from

300°C to 600°C. Phosphor 40 with oxygen fault is fed into vacuum chamber 41 from above by opening the inlet valve 45, and it is dropped little by little. In the middle of vacuum chamber 41, there is provided ozone gas inlet 43 from which ozone gas 43A is fed. Ozone gas 43A is generated by ozone generator 44 as oxygen gas is fed from oxygen cylinder 49. Phosphor 40 with oxygen fault dropping in the chamber is exposed to ozone gas 43A to become phosphor 46 with oxygen fault improved.

[0026]

Next, at least after the treatment in a reduction atmosphere of aluminate phosphors,  $Ba_{(1-x)}Sr_xMgAl_{10}O_{17}\cdot Eu_x$ , the characteristics of phosphors manufactured in each treatment in an ozone atmosphere will be described with reference to the exemplary embodiment.

[0027]

(Exemplary Embodiment 1)

Powders of sufficiently dry and constant-weight barium carbonate ( $BaCO_3$ ), magnesium carbonate ( $MgCO_3$ ), europium oxide ( $Eu_2O_3$ ), and aluminum oxide ( $Al_2O_3$ ) are prepared as the materials. And, these materials are weighed so as to have a molar ratio of constitutive ions of  $Ba:Mg:Eu:Al = 0.99:1.00:0.01:10.00$ . Subsequently, aluminum fluoride as a grain growth accelerator is added to the weighed materials, followed by mixing for 3 hours by using a bowl mill.

[0028]

Next, the mixture is filled into a high-purity alumina crucible and burned at 1200°C for one hour in an ambient atmosphere. After that, the burned mixed powder is burned again at 1200°C for 10 hours in a reduction

atmosphere of nitrogen gas 20% and hydrogen gas 80%. After that, the burned powder is pulverized, dispersed, rinsed, dried, and sieved, and then, treated at 350°C in the chamber in an ozone atmosphere of 7 wt% for one hour by means of the ozone atmosphere treatment device shown in Fig. 2.

[0029]

And, after such a treatment, the powder is rinsed. After the rinsed mixed power phosphor is dehydrated and sufficiently dried, the phosphor is sieved as specified to manufacture a phosphor powder whose common formula is  $\text{Ba}_{0.99}\text{MgAl}_{10}\text{O}_{17}\text{:Eu}_{0.01}$ .

[0030]

Next, the manufactured phosphor powder is irradiated with vacuum ultraviolet ray of 146nm in peak wavelength obtained by a vacuum ultraviolet excimer laser irradiation apparatus (146nm light irradiation apparatus of Ushio Inc.) to measure the luminance with respect to the irradiation time by using luminance meter (LS-110 of Minolta Co., Ltd.). In this invention, as the characteristic value of luminance, the relative luminance value defined hereinafter is set to a performance index. The relative luminance value is obtained by multiplying the relative initial luminance of each phosphor by a luminance sustaining factor. Here, the relative initial luminance is the ratio of the initial luminance of the material in each exemplary embodiment when the initial luminance of a conventional phosphor is 100. Also, the luminance sustaining factor is a percentage obtained by dividing the luminance of the material in each exemplary embodiment after 5000 hours by the initial luminance of the material in each exemplary embodiment. That is, the relative luminance value is for each exemplary embodiment.

the comparison between the conventional phosphor and the phosphor in the exemplary embodiment of the present invention with respect to the luminance of phosphor after lapse of a specific length of time. The material composition ratio, treatment conditions, and relative luminance values are shown in Table 1.

[0031]

(Exemplary Embodiments 2, 3)

With same materials as in the exemplary embodiment 1, the exemplary embodiment 2 is the one whose molar ratio of constitutive ions Ba:Mg:Eu:Al = 0.9:1.0:0.1:10.0, and the exemplary embodiment 3 is the one whose molar ratio thereof is Ba:Mg:Eu:Al = 0.8:1.0:0.2:10.0. The exemplary embodiments 2 and 3 are different from the exemplary embodiment 1 in the following points. In the exemplary embodiment 2, the mixture is burned at 140°C for one hour in an ambient atmosphere and at 1100°C for 10 hours in a reduction atmosphere with nitrogen 95% and hydrogen 5% in partial pressure ratio. In the exemplary embodiment 3, the mixture is burned at 800°C for one hour in an ambient atmosphere and at 1200°C for 10 hours in a reduction atmosphere with nitrogen 100% in partial pressure ratio. And, the phosphor powder manufactured under these conditions is evaluated by relative luminance value the same as in the exemplary embodiment 1. The treatment conditions and relative luminance values are shown in Table 1.

[0032]

(Exemplary Embodiments 4 to 9)

In addition to the material of exemplary embodiment 1, powder of

strontium carbonate ( $\text{SrCO}_3$ ) is prepared, and the exemplary embodiment 4 is the one whose molar ratio of constitutive ions is  $\text{Ba}:\text{Sr}:\text{Mg}:\text{Eu}:\text{Al} = 0.89:0.10:1.00:0.01:10.00$ , and the exemplary embodiment 5 is the one whose molar ratio thereof is  $\text{Ba}:\text{Sr}:\text{Mg}:\text{Eu}:\text{Al} = 0.8:0.1:1.0:0.1:10.0$ , and the exemplary embodiment 6 is the one whose molar ratio thereof is  $\text{Ba}:\text{Sr}:\text{Mg}:\text{Eu}:\text{Al} = 0.7:0.1:1.0:0.2:10.0$ , and the exemplary embodiment 7 is the one whose molar ratio thereof is  $\text{Ba}:\text{Sr}:\text{Mg}:\text{Eu}:\text{Al} = 0.69:0.30:1.00:0.01:10.00$ , and exemplary embodiment 8 is the one whose molar ratio thereof is  $\text{Ba}:\text{Sr}:\text{Mg}:\text{Eu}:\text{Al} = 0.6:0.3:1.0:0.1:10.0$ , and the exemplary embodiment 9 is the one whose molar ratio thereof is  $\text{Ba}:\text{Sr}:\text{Mg}:\text{Eu}:\text{Al} = 0.5:0.3:1.0:0.2:10.0$ . The exemplary embodiments 4 to 9 are different from the exemplary embodiment 1 in the following points. In exemplary embodiment 4, the mixture is not burned in an ambient atmosphere but burned at  $1100^\circ\text{C}$  for 10 hours in a reduction atmosphere of hydrogen 100% in partial pressure ratio. In exemplary embodiment 5, the mixture is burned at  $1300^\circ\text{C}$  for one hour in an ambient atmosphere and at  $1200^\circ\text{C}$  for 10 hours in a reduction atmosphere of nitrogen 99% and hydrogen 1% in partial pressure ratio. In exemplary embodiment 6, the mixture is burned at  $1400^\circ\text{C}$  for one hour in an ambient atmosphere and at  $1400^\circ\text{C}$  for 10 hours in a reduction atmosphere of nitrogen 90% and hydrogen 10% in partial pressure ratio. In exemplary embodiment 7, the mixture is burned at  $1300^\circ\text{C}$  for one hour in an ambient atmosphere and at  $1300^\circ\text{C}$  for 10 hours in a reduction atmosphere of nitrogen 98% and hydrogen 2% in partial pressure ratio. In exemplary embodiment 8, the mixture is burned at  $1000^\circ\text{C}$  for one hour in an ambient atmosphere and at  $1300^\circ\text{C}$  for 10

hours in a reduction atmosphere of nitrogen 90% and hydrogen 10% in partial pressure ratio. In exemplary embodiment 9, the mixture is burned at 1200°C for one hour in an ambient temperature and at 1300°C for 10 hours in a reduction atmosphere of nitrogen 50% and hydrogen 50% in partial pressure ratio. And, the phosphor powders manufactured under these conditions are evaluated by relative luminance value the same as in the exemplary embodiment 1. The treatment conditions, relative luminance values, and other results are shown in Table 1.

[0033]

(Comparative example)

As a comparative example, a phosphor whose molar ratio of constitutive ions is same as in the exemplary embodiment 5 is manufactured by a conventional manufacturing method (conventional phosphor). The difference from the exemplary embodiment 5 is that a step of treatment in an ozone atmosphere for improving oxygen fault is not included. The luminance sustaining rate of the example is 69%, and therefore, the relative luminance value is 69.

[0034]

[Table 1]

	Constitutive molar ratio			General formula	Ambient atmosphere temp.	Reduction atmosphere	Ozone atmosphere	Relative luminance value
	Ba	Sr	Eu			Temp. H <sub>2</sub> conc.	Temp. O <sub>3</sub> conc.	
Exemplary Embodiment 1	0.99	0	0.01	Ba <sub>0.99</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.01</sub>	1200°C	1200°C, 80%	350°C, 7%	73
Exemplary Embodiment 2	0.9	0	0.1	Ba <sub>0.9</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.1</sub>	1400	1100 , 5		92
Exemplary Embodiment 3	0.8	0	0.2	Ba <sub>0.8</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.2</sub>	800	1200 , 0		88
Exemplary Embodiment 4	0.89	0.1	0.01	Ba <sub>0.89</sub> Sr <sub>0.1</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.01</sub>	—	1100 , 100		72
Exemplary Embodiment 5	0.8	0.1	0.1	Ba <sub>0.8</sub> Sr <sub>0.1</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.1</sub>	1300	1200 , 1		89
Exemplary Embodiment 6	0.7	0.1	0.2	Ba <sub>0.7</sub> Sr <sub>0.1</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.2</sub>	1400	1400 , 10		91
Exemplary Embodiment 7	0.69	0.3	0.01	Ba <sub>0.69</sub> Sr <sub>0.3</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.01</sub>	1300	1300 , 2		75
Exemplary Embodiment 8	0.6	0.3	0.1	Ba <sub>0.6</sub> Sr <sub>0.3</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.1</sub>	1000	1300 , 10		90
Exemplary Embodiment 9	0.5	0.3	0.2	Ba <sub>0.5</sub> Sr <sub>0.3</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.2</sub>	1200	1300 , 50		74
Comparative example	0.8	0.1	0.1	Ba <sub>0.8</sub> Sr <sub>0.1</sub> MgAl <sub>10</sub> O <sub>17</sub> :Eu <sub>0.1</sub>	1300	1200 , 1	—	69

[0035]

As is obvious in Table 1, in aluminate phosphor Ba<sub>(1-x-y)</sub>Sr<sub>y</sub>MgAl<sub>10</sub>O<sub>17</sub>:Eu<sub>x</sub> (where  $0.01 \leq x \leq 0.20$ ,  $0 \leq y \leq 0.30$ ), the relative luminance value is improved by 14 on an average as compared with the comparative example, conventional phosphor, showing that it is improved in luminance. In exemplary embodiments 1 to 9, the burning conditions in reduction atmosphere related with the specimen prepared and the burning conditions in ambient atmosphere preceding thereto are varied, but whether or not the

treatment in an ozone atmosphere is performed is probably more important factor closely related to the difference in relative luminance value rather than the influence to the relative luminance value caused due to the variation of the conditions. Particularly, they are same in molar ratio of constitutive ions, and different from each other only with respect to the treatment in ozone atmosphere for improving oxygen fault, because the difference in relative luminance value is 20 between the exemplary embodiment 5 and the comparative example. Further, the effect of treatment in ozone atmosphere can be inferred from the fact in the following.

[0036]

Firstly, Eu is often used as an activator that may become bivalent or trivalent in general, but in the example of BAM type that is a blue phosphor, it is necessary to substitute bivalent Ba with bivalent Eu to make stable luminescence center  $\text{Eu}^{2+}$  while producing the base crystal of  $\text{Ba}_{(1-x)}\text{MgAl}_{10}\text{O}_{17}$  from its material. As a conventional basic burning method to achieve the purpose, it is preferable to burn the phosphor at high temperatures ranging from 1000°C to 1500°C for 4 hours or over in a proper reduction atmosphere.

[0037]

Secondly, as for oxygen fault improvement of base crystal generated in the reduction atmosphere, when the phosphor is continuously treated at 350°C to 400°C in an ozone atmosphere, the effect of improving the oxygen fault can be confirmed.

[0038]

Also, Sr is not always necessary to be contained in the composition of phosphor, but when Sr is contained, Sr<sup>2+</sup> being smaller in ion radius is substituted in part for a part of Ba<sup>2+</sup>, and the grid constant of crystal structure is a little decreased and it is possible to make the emission color of the blue phosphor closer to the desired color.

[0039]

Next, Fig. 3 is a perspective view of an essential part of a plasma display unit in the preferred embodiment of the present invention. Front panel PA1 is formed with transparent insulating front substrate 11 on which display electrode 15 formed of scanning electrode 12a and sustaining electrode 12b, and dielectric layer 13 to cover them are formed, and further, protective layer 14 is formed on dielectric layer 13.

[0040]

Display electrode 15 has specific pitches on front substrate 11, and a predetermined number of electrodes are formed. Also, dielectric layer 13 is required to be formed after display electrode 15 and to completely cover the display electrode 15, which is therefore formed by printing or burning low-melting point glass in general. As a glass paste material, for example, it is possible to use low-melting point glass paste having a so-called (PbO-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>-ZnO-BaO) type glass composition, including lead oxide (PbO), silicon oxide (SiO<sub>2</sub>), boron oxide (B<sub>2</sub>O<sub>3</sub>), zinc oxide (ZnO) and barium oxide (BaO). By using the glass paste, for example, screen printing and burning are repeated to obtain dielectric layer 13 having a predetermined film thickness. The film thickness can be set according to the thickness of display electrode 15 and the intended electrostatic capacity value. In the

preferred embodiment of the present invention, the film thickness of dielectric layer 13 is about 40  $\mu$ m. Further, it is possible to use glass paste based on at least one of lead oxide (PbO), bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) and phosphorus oxide (PO<sub>4</sub>).

[0041]

Also, protective layer 14 is disposed to make dielectric layer 13 free from sputtering due to plasma discharge, and is required to be an excellent material having anti-sputtering property. Accordingly, magnesium oxide (MgO) is often used.

[0042]

On the other hand, data electrode 17 for writing image data is formed on rear substrate 16 which is transparent and insulative in a direction perpendicular to display electrode 15 of front panel PA1. After insulator layer 18 is formed on rear substrate 16 in such manner as to cover the data electrode 17, barrier 19 is formed in parallel with the data electrode 17 and nearly in the middle between data electrodes 17. Also, phosphor layer 20 is formed on a region between barriers 19, thereby forming rear panel PA2. Phosphor layer 20 is formed adjacent to phosphors emitting R light, G light and B light which configure pixels.

[0043]

Data electrode 17 is formed by thin film forming technology such as printing, burning or sputtering method that is employed for forming a laminated film structure such as a single-layer film structure of silver, aluminum or copper of low resistance or a two-layer structure of chromium and copper, and a three-layer structure of chromium, copper and chromium.

Also, insulator layer 18 can be formed by using the same material and film-forming method as for dielectric layer 13. Further, it is also preferable to use a glass paste based on at least one of lead oxide (PbO), bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>) and phosphorus oxide (PO<sub>4</sub>). Phosphors manufactured by the above manufacturing method which respectively emit R light, G light and B light are applied, for example, by an ink jet method to areas surrounded by barriers 19, thereby forming phosphor layer 20.

[0044]

With front panel PA1 and rear panel PA2 opposed to each other, barrier 19, protective layer 14 on front substrate 11, and discharge space 30 surrounded by phosphor layer 20 on rear substrate 16 are formed. Mixed gas of Ne and Xe is filled into the discharge space 30 under the pressure of about 66.5 kPa, and AC voltage ranging from 20 or 30 kHz to 200 or 300 kHz is applied between scanning electrode 12a and sustaining electrode 12b for the purpose of discharge, and thereby, phosphor layer 20 can be excited by ultraviolet ray generated when excited Xe atom returns to its basic state. Due to the excitation, phosphor layer 20 emits R light, G light or B light according to the material coated, and therefore, selecting the pixels and color for emission of light by data electrode 17, it is possible for the predetermined pixel portion to emit the necessary light and to display color images.

[0045]

Fig. 4 is a graph showing the luminance variation factor of the phosphor used in the plasma display unit. A pulse voltage of 180V amplitude and 15kHz frequency is applied between display electrodes 15,

and the phosphor of exemplary embodiment 5 manufactured in the preferred embodiment of the present invention is compared with the phosphor of comparative example manufactured by the conventional method, and shown is the secular change of the luminance. The luminance in the initial lighting being 100%, the luminance variation factor corresponds to a value obtained by dividing the luminance in each lighting time by the luminance in the initial lighting. As for the luminance variation factor in 5000 hours lighting, the luminance decreases to 72% in the case of the phosphor manufactured by the conventional method, while in the case of the phosphor manufactured in the preferred embodiment of the present invention, 84% luminance is maintained. It shows 12% improvement in luminance variation factor alone, suppressing the luminance deterioration. The phosphor manufacture by the manufacturing method in the preferred embodiment of the present invention is treated in an ozone atmosphere after burning in a reduction atmosphere, and therefore, it is less in oxygen fault in the crystal structure of the phosphor and also less in non-crystal structure. As a result, it is less in deterioration of crystal structure and luminance even in case of ultraviolet ray irradiation and ion impact.

[0046]

In this preferred embodiment,  $\text{Eu}^{2+}$  is used as an activator of BAM type in the description, but in the case of  $\text{CaMgSi}_2\text{O}_6:\text{Eu}$  using  $\text{Eu}^{2+}$  of other type as an activator, and green phosphor  $(\text{Ba, Sr, Mg})\text{O} \cdot a\text{Al}_2\text{O}_3:\text{Mn}$  having oxide as base crystal and using  $\text{Mn}^{2+}$  as an activator, it is also possible to assure excellent luminance due to the treatment in ozone atmosphere and to obtain an effect of suppressing luminance deterioration.

[0047]

## [Advantages of the Invention]

As described above, the method of manufacturing a phosphor of the present invention is a method of manufacturing a phosphor having a luminescence center that is at least one of Eu and Mn added as an activator and base crystal that is composite oxide containing at least one of elements such as Ba, Ca, Sr, and Mg, at least comprising a step of treatment in a reduction atmosphere for burning a mixed material of the phosphor in a reduction atmosphere by once at least; and a step of treatment in an ozone atmosphere for treating the mixed material in an ozone atmosphere which is executed after the step of the treatment in a reduction atmosphere. Due to such a manufacturing method, even in the case of a phosphor having oxide as base crystal which requires bivalent activation of Eu or Mn that is luminescence center, it is possible to provide a phosphor manufacturing method capable of improving oxygen fault without lowering the luminance, a phosphor being excellent in luminance and less in luminance deterioration, and a plasma display unit using the same.

## [Brief Description of the Drawings]

Fig. 1 is a flow chart showing a method of manufacturing a phosphor in the preferred embodiment of the present invention.

Fig. 2 is a sectional view of a treatment apparatus in the step of treatment in an ozone atmosphere in the preferred embodiment of the present invention.

Fig. 3 is a perspective view of an essential portion of a plasma display unit in the preferred embodiment of the present invention.

Fig. 4 is a graph showing the luminance variation factor of a phosphor used in the plasma display unit in the preferred embodiment of the present invention.

[Description of the Reference Numerals and Signs]

- 11 Front substrate
- 12a Scanning electrode
- 12b Sustaining electrode
- 13 Dielectric layer
- 14 Protective layer
- 15 Display electrode
- 16 Rear substrate
- 17 Data electrode
- 18 Insulator layer
- 19 Barrier
- 20 Phosphor layer
- 30 Discharge space
- 40 Phosphor with oxygen fault
- 41 Vacuum chamber
- 42 Heater
- 43 Ozone gas inlet
- 43A Ozone gas
- 44 Ozone generator
- 45 Feed valve
- 46 Phosphor with oxygen fault improved
- 49 Oxygen cylinder

**PA1** Front panel

**PA2** Rear panel

[Name of the Document] Abstract

[Abstract]

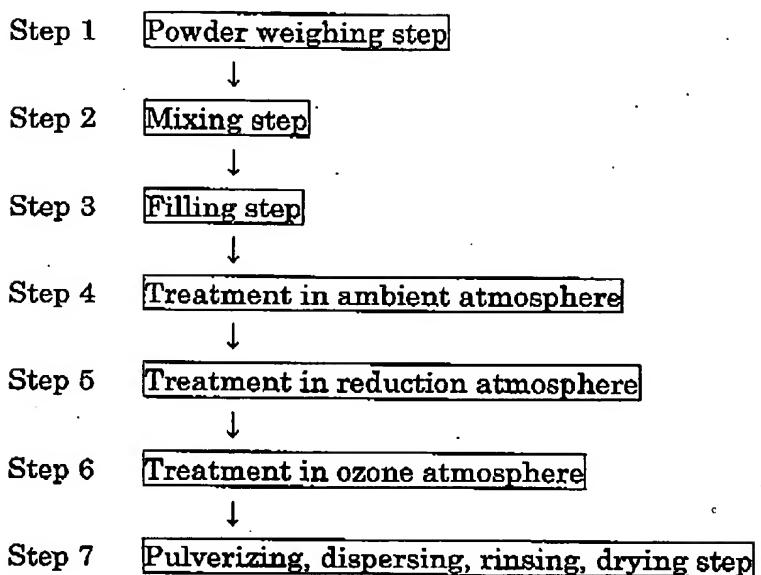
[Problem] In a phosphor whose base crystal is composed of oxide, oxygen atoms are taken away from the base crystal due to burning in a reduction atmosphere, causing oxygen fault in the phosphor to be increased.

[Means to Solve the Problem] After weighing, mixing, and filling of phosphor powder, it includes a step of burning in a reduction atmosphere by once at least and a step of treatment in an ozone atmosphere for pulverizing, dispersing, rinsing, and drying in an ozone atmosphere after the last treatment in a reduction atmosphere, thereby improving oxygen fault of the base crystal.

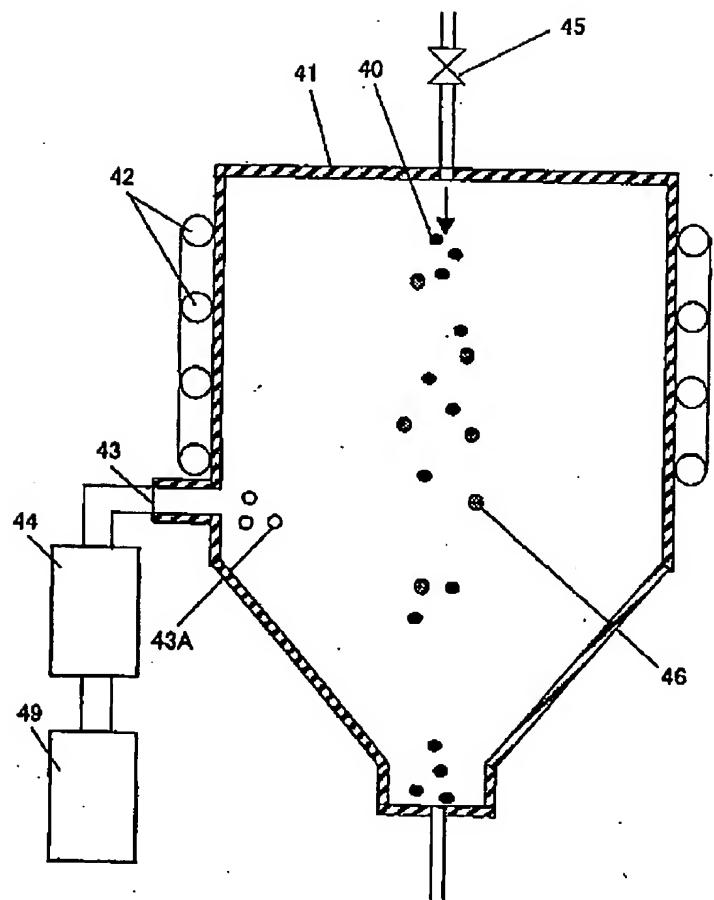
[Selected Drawing] Fig. 1

[Name of the Document] Drawing

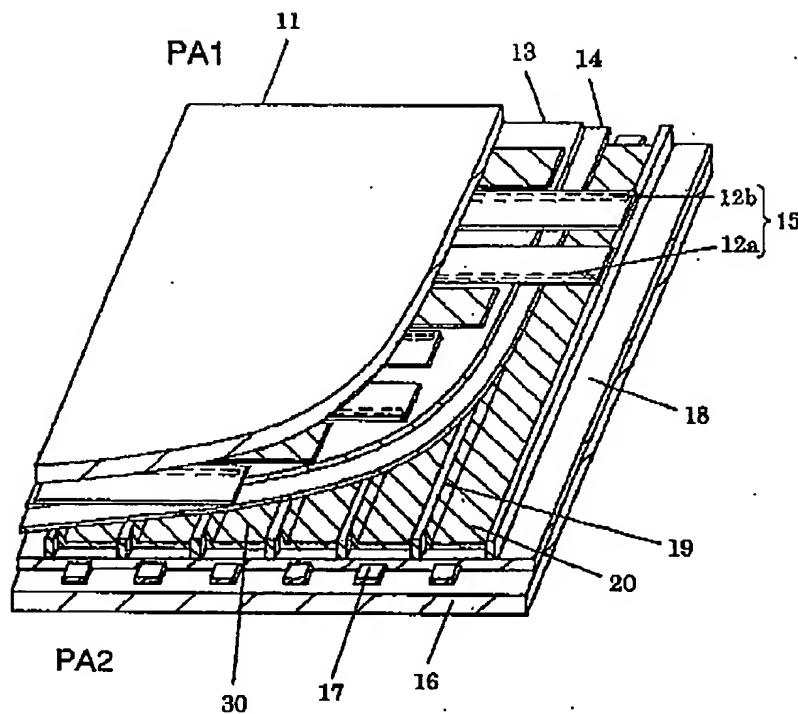
[Fig. 1]



[Fig. 2]



[Fig. 3]



[Fig. 4]

